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TITLE: COMPARISON OF SURFACE MODIFICATIONS OF POLY(ETHER URETHANES) BY CHEMICAL INFUSION AND GRAFT POLYMERIZATION

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COMPARISON OF SURFACE MODIFICATIONS OF POLY(ETHER URETHANES) BY CHEMICAL INFUSION AND GRAFT POLYMERIZATION

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INTRODUCTION

Because of their good elastomeric properties including the ability to undergo repeated flexing without failure, polyurethanes are used in a number of biomedical applications including flexing diaphragms or coatings on surfaces in artificial hearts and heart assist devices. In particular, the poly(ether urethanes) are preferred for use in biomedical applications because of their greater hydrolytic stability as compared to poly(ester urethanes). However, poly(ether urethanes), as other polymeric materials in contact with blood, cause formation of thrombus[1] and bacterial infections[2]. These problems might be overcome by incorporation of antithrombogenic substances and/or antibacterial agents in the surface of the polymer.

One of our approaches to surface modification uses the chemical infusion process[3] to introduce materials into the outermost layer of the polymeric material, thereby altering the surface without changing the bulk properties of the polymer. The infused materials may slowly diffuse out of the infusion layer if they are volatile or highly mobile. However if polymeric infusant materials are employed, they may become chain entangled with the host polymer and result in a permanently modified surface. A second approach utilizes photo-initiated graft polymerization[4] of poly(ether urethanes) with an appropriate monomer. We have explored both of these methods by examining the infusion of polyvinylpyrrolidone (PVP) and poly(ethylene glycol) (PEG) into commercially available poly(ether urethanes) and the graft polymerization of N-vinyl pyrrolidone onto poly(ether urethanes). Preliminary results are presented here.

EXPERIMENTAL

Materials and methods:

Tecoflex EG-60D and Pellethane 2363-65D were obtained from Thermedics, Inc. and Dow Chemical Co., respectively. The poly(ether urethanes) were injection molded into a disk shape, 26 mm in diameter and 3.2 mm thick. The diameter was machined back to 22.2 mm and cleaned in an Alconox detergent solution followed by several rinses with deionized water. The samples were air dried at 35°C prior to use. Samples for contact angle measurements were cut into a square shape 12 X 12 mm and cleaned as above.

PVP (MW 10,000), Plasdone C15, was obtained from GAF. Poly(ethylene glycol) (MW 3,400), N-vinyl pyrrolidone (NVP), vinyl sulfonic acid (sodium salt), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and dirheniumdecacarbonyl ($Re_2(CO)_{10}$) were purchased from Aldrich Chemical, Co. NVP was purified by vacuum distillation and zone refining. $Re_2(CO)_{10}$ was sublimed at 40°C prior to use. Baker reagent grade isopropyl alcohol (IPA) and HPLC grade chloroform and

Burdick & Jackson acetonitrile (distilled in glass) were used as received.

The contact angles were measured by the sessile drop method[5] and the Wilhelmy technique[6]. The former method consisted of direct measurement of the dimensions of a drop of water on the sample. A Nikon Profile Projector model H-14B was used to rapidly measure the dimensions of a 0.4 μl drop of deionized water before evaporation occurred. Several drops were measured on both sides of a given sample and averaged. For the Wilhelmy technique, the "WET-TEK", CAHN, Surface Force Analyzer-211 was used to obtain receding and advancing contact angles. The surface tension of the deionized water was determined and used in the contact angle calculations. Measurements were repeated after 1, 4, 24 and 48 hours in deionized water to determine the effect of hydration.

Procedure:

The infusion chamber (pictured in Figure 1) consists of two glass tubes connected by flexible tubing. One tube is stirred, or may be filled with glass beads for static stirring, to ensure complete mixing while the other holds the samples. The system uses a peristaltic pump to circulate the solution and a second metering pump to add the diluent solution to the system in small increments. In this manner the solution in the apparatus gradually becomes richer in diluent. The diluent solution was prepared from varying amounts of polymer such as PVP in IPA. The starting solution was prepared as 25% chloroform in the diluent solution. A total volume of 325 mL required about 7 hours dilution time at a dilution rate of 2 mL/min for complete dilution of the solution. The samples were rinsed with IPA upon removal from the final solution.

The graft polymerization of poly(ether urethanes) is based on the method of Bamford and coworkers[4]. The urethane nitrogen was brominated by treatment of the sample with an aqueous solution of KOBr. After rinsing in deionized water, the samples were dried. A solution of $Re_2(CO)_{10}$ (1×10^{-3} M) and NVP (1.0 M) in acetonitrile was placed in a Pyrex tube and purged with argon. Samples mounted in a string of retaining clips were placed in the solution as purging continued for 5 minutes. The apparatus was irradiated with an unfiltered UV source centered at 366 nm for a minimum of one hour. The grafted samples were rinsed with deionized water and dried in a cool (35°C) oven.

The blood testing chamber has been previously described.[3] Flat disks of the material of interest are placed in the bottom of the Teflon ports and an inner sleeve of Tecoflex is placed in the port to secure the disk. Aliquots of suspensions of cellular constituents may be added to the chamber at 37°C with agitation to determine adhesion of blood factors. Adhesion of platelets, polymorphonuclear leukocytes and blood proteins will be examined.

RESULTS AND DISCUSSION

Our previous study[3] of the chemical infusion of poly(methylmethacrylate) (PMMA) with PVP indicated promising results in that a decrease in the adherence of PMN leukocytes in comparison to untreated samples was observed. Since poly(ether urethanes) have been used in a number of biomedical applications, we decided to investigate the application of the chemical infusion technique in modifying the surfaces of commercially available poly(ether urethanes). Tecoflex and Pellethane were chosen because of

their ease of fabrication into test specimens. The hydrophilic polymers, PVP and PEG, were chosen as infusant materials because they should modify the surface energy of the treated sample and, hopefully, improve the blood compatibility of the polymer. We have infused diluent solutions containing from 5% to 30% by weight polymer and examined the differences in contact angles. By increasing the amount of PVP in the treatment solution, a decrease in the contact angle is shown in Table 1.

A second method of surface modification is the graft polymerzation of poly(ether urethanes). This method has been used to graft vinylic monomers on commercial poly(ether urethanes)[4]. This requires bromination of the urethane nitrogen with an aqueous solution of KOBr (Equation 1)

$$\text{R-NH-COO-R'} \xrightarrow{+\ \text{KOBr(aq)}} \text{R-NBr-COO-R'} \qquad (1)$$

followed by graft polymerization. The graft polymerization uses $Re_2(CO)_{10}$ as the photo-initiation catalyst to selectively graft at the urethane nitrogen. Appropriate monomers include compounds containing a vinylic group such as N-vinyl pyrrolidone(NVP), vinyl sulfonic acid (sodium salt) or 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS). NVP represents covalent attachment of PVP onto the substrate, while the latter two represent introduction of charged polymer chains on the surface of the substrate. Grafting of these monomers onto poly(ether urethanes) will significantly change the surface energy. This can be seen in a decrease in the measured contact angle for NVP grafted Tecoflex (Table 1) when compared to untreated Tecoflex.

These preliminary results indicate that both techniques increase the hydrophilicity of the poly(ether urethane) surface. A more detailed study comparing the contact angles of infusion treated samples and grafted samples will be presented along with a comparison of the two methods used to measure contact angles. In addition, characterization of the surfaces by SEM, optical microscopy, and adhesion of selected blood factors will be presented. Because iodine and silver nitrate form complexes with PVP[7] in solution, PVP-I and PVP-$AgNO_3$ will be incorporated into poly(ether urethanes) by the chemical infusion process. This has a two-fold purpose: to aid in analytical evaluation of the incorporation of the polymer in the surface and to incorporate an additive into the surface that may potentially have antibacterial properties. An evaluation of these properties will be presented.

Table 1 COMPARISON OF CONTACT ANGLES FOR PVP-INFUSION TREATED AND GRAFTED TECOFLEX SAMPLES

Sample (% in Diluent)/(Graft time)	θ_{ave} (degree) Sessile drop	Wilhelmy
untreated	88.9	75.6
PVP (5%)	67.9	70.6
PVP (10%)	67.5	66.9
PVP (20%)	61.0	64.9
PVP (30%)	59.0	62.2
Graft (1hr)	72.8	54.2

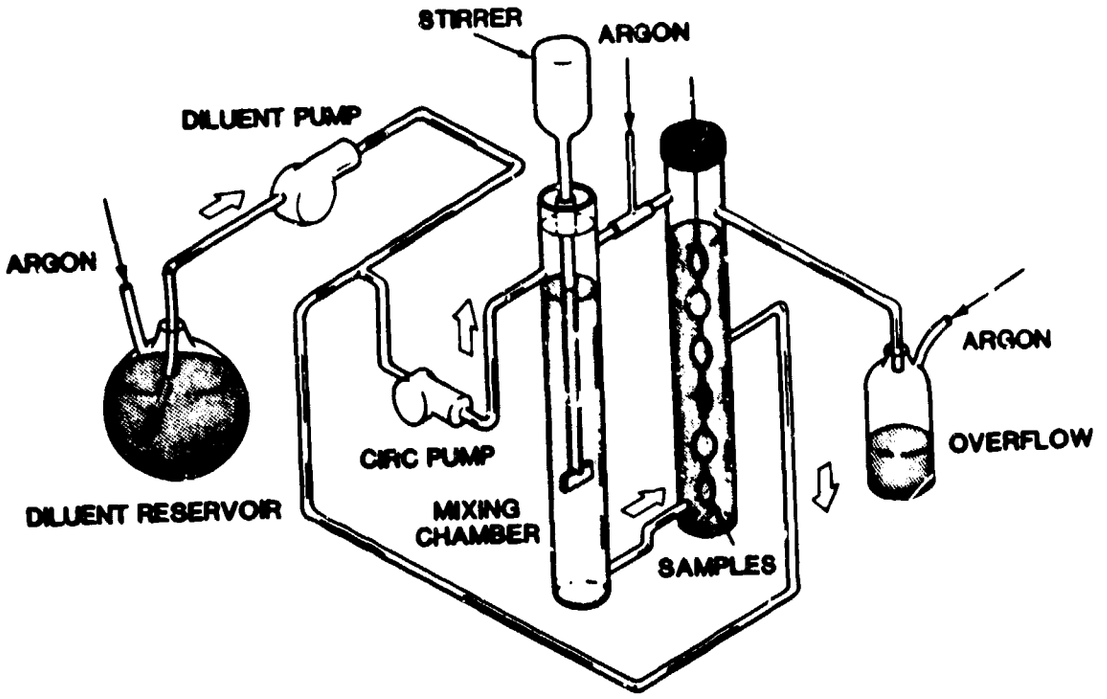

Figure 1 Schematic of the Chemical Infusion Apparatus

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